Recoil Reactions in the Irradiated Tris-(ethylenediamine)-cobalt(III) Complexes

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It was previously reported[1] that the outer anions might play an important role in the radiocobalt recoil reactions in the neutron-irradiated hexammine- and aquopentammine cobalt(III) complexes. For the purpose of confirming such effects of outer anions, the present authors have investigated a similar system, a group of tris-(ethylenediamine)-cobalt(III) complexes containing various outer anions, of which only the nitrate and bromide have been studied before.[2-4]

The five kinds of complex compounds listed in Table I were irradiated with slow neutrons in JRR-1 reactor for 1 hr. at pile temperature in the presence of air. The neutron flux was estimated to be approximately 3×10^{11} n/cm²·sec. After it had been stored in dry ice for one to three days, the irradiated salt was dissolved in distilled water and the ^{60}Co-labeled species present in the aqueous solutions were separated by means of paper electrophoresis, ion-exchange, precipitation, or recrystallization. The results are summarized in Table I. The dependence of the retention value and of the *S*-value** of the tris-(ethylenediamine)-cobalt complexes upon the stability as ligands of the outer anions are shown in Figs. 1 and 2 respectively. For convenience of discussion, the retention value and the *S*-value for hexammine- and aquopentammine-cobalt(III) complexes[1] are also shown together.

As may be seen in Fig. 1, the retention in the three systems generally tends to increase with a decrease in the stability of the outer anion as a ligand. Namely, the restoration of parent chemical forms may be more favored in the salt containing less stable outer anions. Figure 2 indicates that the *S*-value in the three systems increases in almost the same

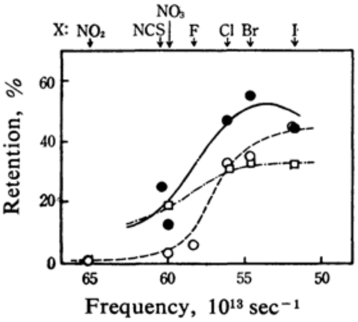

Fig. 1. The relationship between retention and frequency of the maximum in the first absorption band of $Co(NH_3)_5X$.

—●— $[Co(en)_3]X_3$

--○-- $[Co(NH_3)_6]X_3$

-·□-· $[Co(NH_3)_5H_2O]X_3$

TABLE I. PERCENTAGE DISTRIBUTION OF ^{60}CO-LABELED SPECIES IN THE IRRADIATED TRIS-(ETHYLENEDIAMINE)-COBALT(III) COMPLEXES

Target	^{60}Co-labeled species, %*1						
	$Co\,en_3^{3+}$ *2	$Co\,en_2a_2^{3+}$	$Co\,en_2aX^{2+}$	$Co\,en_2X_2^{+}$	Co^{2+}	Neutral species	Anionic species
$[Co(en)_3](NCS)_3$	24.8	2.5	2.9	1.4	53.9	3.8	13.0*3
$[Co(en)_3](NO_3)_3$	12.2	6.0	7.0	1.4	69.4	1.8	1.4
$[Co(en)_3]Cl_3\cdot3\,H_2O$	47.3	13.8	10.7	1.8	23.7	1.3	0.1
$[Co(en)_3]Br_3\cdot3\,H_2O$	55.0	10.0	4.5	0.9	28.8	1.3	0.5
$[Co(en)_3]I_3\cdot H_2O$	44.0	4.0	7.7	1.1	41.1	0.3	—

*1 $a=H_2O$

*2 Retention, or labeled chemical species (%) identical with the target.

*3 Attributed to some unidentified ^{60}Co-labeled anionic species.

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** $S=\dfrac{[\text{Sum of percentages of }^{60}\text{Co-labeled complexes containing more anionic ligands than the target}]}{[\text{Sum of percentages of all }^{60}\text{Co-labeled complexes}]}$

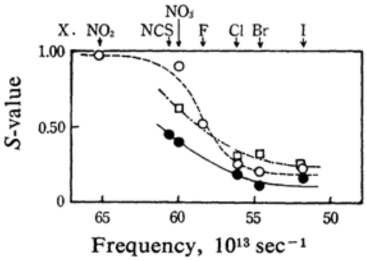

Fig. 2. The relationship between S-value and frequency of the maximum in the first absorption band of $Co(NH_3)_5X$.
—●— $[Co(en)_3]X_3$
--○-- $[Co(NH_3)_6]X_3$
-·□-· $[Co(NH_3)_5H_2O]X_3$

manner with the increasing stability of the outer anion as ligand, and thus the incorporation of outer anions into ligands seems to be more favored in the salt containing more stable outer anions. This dependence of the retention value and the S-value on the stability of the outer anion may be generally explained by assuming that the outer anions and ligand groups (NH_3, ethylenediamine, or H_2O molecules), more or less ruptured as a result of recoil, compete with each other in the subsequent reactions, during which various ^{60}Co-labeled complexes are formed through the reactions of recoil cobalt atoms with neighboring entities according to their concentrations and stabilities as complexed with cobalt.

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